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Polypropylene–clay composite prepared from Indian bentonite

MADHUCHHANDA SARKAR, KAUSIK DANA*, SANKAR GHATAK and AMARNATH BANERJEE[†]

Clay & Traditional Ceramics Division, Central Glass and Ceramic Research Institute, Kolkata 700 032, India

[†]Department of Polymer Science and Technology, University of Calcutta, Kolkata 700 009, India

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Abstract. In the present work, a set of experimental polypropylene (PP) clay composites containing pristine bentonite clay of Indian origin has been prepared and then characterized. The polymer clay composites are processed by solution mixing of polypropylene with bentonite clay using a solvent xylene and high speed electric stirrer at a temperature around 130°C and then by compression molding at 170°C. The mechanical properties of PP–clay composites like tensile strength, hardness and impact resistance have been investigated. Microstructural studies were carried out using scanning electron microscope and transmission electron microscope and the thermal properties were studied using differential scanning calorimeter. Mechanical properties of the prepared composites showed highest reinforcing and toughening effects of the clay filler at a loading of only 5 mass % in PP matrix. Tensile strength was observed to be highest in case of 5 mass % of clay loading and it was more than 14% of that of the neat PP, while toughness increased by more than 80%. Bentonite clay–PP composite (5 mass %) also showed 60% increase in impact energy value. However, no significant change was observed in case of hardness and tensile modulus. Higher percentages of bentonite clay did not further improve the properties with respect to pristine polypropylene. The study of the microstructure of the prepared polymer layered silicate clay composites showed a mixed morphology with multiple stacks of clay layers and tactoids of different thicknesses.

Keywords. Layered silicate; smectites; polymer clay composite; bentonite; polypropylene; characterization.

1. Introduction

Polymers can be reinforced with different fillers, which enhance the mechanical properties of the virgin polymer. Conventional fillers like talc, mica, CaCO₃, kaolin, fumed silica and glass fibre have been found to increase mechanical properties with detrimental impact on density, transparency and processability (Lei *et al* 2006). In recent years, polymer based nanocomposites have attracted increased attention, both in industry and academia. The most common nano-sized fillers are carbon nanotubes, nanosized particles and intercalated layers. Since nanoparticles have significant surface, size and quantum effects, their incorporation in polymer matrix improves several material properties. These include high elastic modulus, lower gas permeability, increased strength and lower flammability, increased biodegradability etc (Ginzburg *et al* 2000). The large varieties of polymer systems which are used in the preparation of polymer-layered silicates (PLS) nanocomposites are vinyl polymers, condensation (step) polymers, polyolefins like polypropylene (PP), polyethylene, polyethylene oligomers, speciality poly-

mers and biodegradable polymers (Sinha Ray and Okamoto 2003). Among PLS nanocomposites, those based on PP attracted more interest because PP is one of the most widely used and fastest growing thermoplastics. PLS nanocomposites have recently found applications in packaging, automotive, aerospace and electronics industries (Kato *et al* 1997; Usuki *et al* 1997; Giannelis 1998; Oya *et al* 2000; Biswas and Sinha Ray 2001). In general, polymer/layered silicate nanocomposites are of three different types, viz. (i) intercalated nanocomposites, for which insertion of polymer chains into a layered silicate structure occurs in a crystallographically regular fashion, with a repeat distance of few nanometers, regardless of polymer to clay ratio, (ii) flocculated nanocomposites, for which intercalated and stacked silicate layers flocculated to some extent due to the hydroxylated edge–edge interactions of the silicate layers, and (iii) exfoliated nanocomposites, for which the individual silicate layers are separated in the polymer matrix by average distances that depend only on the clay loading. A number of PLS nanocomposites preparation methods have been reported in the literature. The three most common methods to synthesize PLS nanocomposites are intercalation of a suitable monomer and subsequent *in situ* polymerization, intercalation of polymer from solution and polymer melt intercalation (Nguyen and Baird 2006).

*Author for correspondence (kdana@cgcricri.res.in)

The swelling clays belonging to 2 : 1 layered clays are commonly used for the preparation of polymer layered silicate nanocomposites. Montmorillonite, hectorite and saponite are the most commonly used layered silicates in filled-polymer nanocomposites (Park *et al* 2002). The clay used in this work is sodium bentonite because of its natural abundance and low cost. Bentonites are defined as a sedimentary rock consisting of a large portion of expandable clay minerals with three-layer structures (smectites) such as montmorillonites (80%), beidellite, nontronite etc with minor amounts of non-clay minerals such as quartz, calcite, dolomite and feldspar (Grim 1968).

In this present study, PP-clay composites have been prepared with PP and an unmodified sodium bentonite clay of Indian origin (Kuch, Gujarat). PP-clay composites are prepared with three different percentages (5%, 7.5% and 10%) of clay and their physical properties and micro-structures have been investigated.

2. Experimental

2.1 Materials

PP homopolymer (H030SG) supplied by M/s Reliance Industries Ltd., having an MFI of 3 was used in this work. Unmodified bentonite clay of Indian origin (Kuch, Gujarat) was used as filler and xylene (L.R. grade, International Chemicals) was used as a solvent.

2.2 Characterization of clay

The clay was chemically analysed. Gravimetric method was used to determine SiO_2 and Al_2O_3 whereas Fe_2O_3 , CaO and MgO were estimated volumetrically. Alkalis were determined by flame photometry. Loss on ignition (LOI) was determined by heating the sample at 1000°C for 60 min and recording the % weight loss.

Particle size analysis of the clay bentonite was carried out in a particle size analyser (Mastersizer 2000 MU, Malvern) and the results confirmed the distribution of the particle size in this clay. Particle size distribution of the clay was obtained by dispersing the clay in water and then ultrasonicated the clay. BET surface area of the clay was investigated by Sorptly -1750 (Carlo Erba Instrumentazione).

The bentonite clay was characterized by X-ray diffraction using Philips 'X-pert Pro' diffraction unit attached with secondary monochromator, automatic divergence slit and nickel filter which had a $\text{CuK}\alpha$ radiation source operated at a generator voltage, 45 kV and current, 40 μA . The instrument was run at step scan mode within 2θ angle 5° to 45° . The collected data was refined using Profit software. For reliability of data, each sample was scanned several times.

DTA-TGA study of clay has been done by NETZSCH STA 409C, which is a simultaneous thermal analyser. The study was done with reference to alumina within the temperature range 45 – 1030°C with a scan rate of $10^\circ\text{C}/\text{min}$.

2.3 Preparation of polypropylene-bentonite clay composites

For preparing polypropylene bentonite clay composites, the clay was dried in an oven at a temperature of 75°C for 24 h. Three compositions (table 1) were prepared with varying clay contents. Clay is accurately weighed and mixed with the polypropylene matrix in a solution mixing process using xylene as the solvent. Solvent xylene was added to a 1000 ml beaker containing PP. The heating mantle was heated to around 130°C . Heating was continued until all PP granules dissolved and a clear solution resulted. The solvent containing PP was initially shaken by hand vigorously and then stirred by high speed electrical stirrer keeping the beaker in heating condition. The clay dispersed in xylene was added slowly to PP and xylene mixture. Vigorous and continuous stirring helped uniform dispersion of clay as well as intercalation of PP into clay layers. The beaker was kept open for a few hours for evaporation of xylene. Then the prepared polymer clay composite was broken mechanically and mixed well. After complete evaporation of xylene, the composite samples were prepared by compression molding at 170°C temperature, 10 Psi pressure with 1 h duration.

2.4 Characterization of prepared clay composites

For X-ray diffraction study of the composite sample as well as pristine PP samples, Philips 'X-Pert Pro' diffraction unit was run at a step scan mode within 2θ angle 10 – 70° .

Mechanical properties of the prepared polymer clay composites were investigated. Tensile properties were investigated by using the Universal Tensile Testing machine (Instron 3344, series IV) operating at a crosshead speed of 30 mm/min at a temperature of 25°C . Samples were prepared by compression molding of prepared clay composite at 170°C in a form of a sheet from which test specimens were cut using a type III die according to ASTM D 638. Izod impact test was done using an Izod Impactometer at room temperature. The samples for Izod were

Table 1. Batch composition of PP-clay composites.

Batch code	PP (mass %)	Clay (mass %)
PP	100	0
PP5C	100	5
PP7.5C	100	7.5
PP10C	100	10

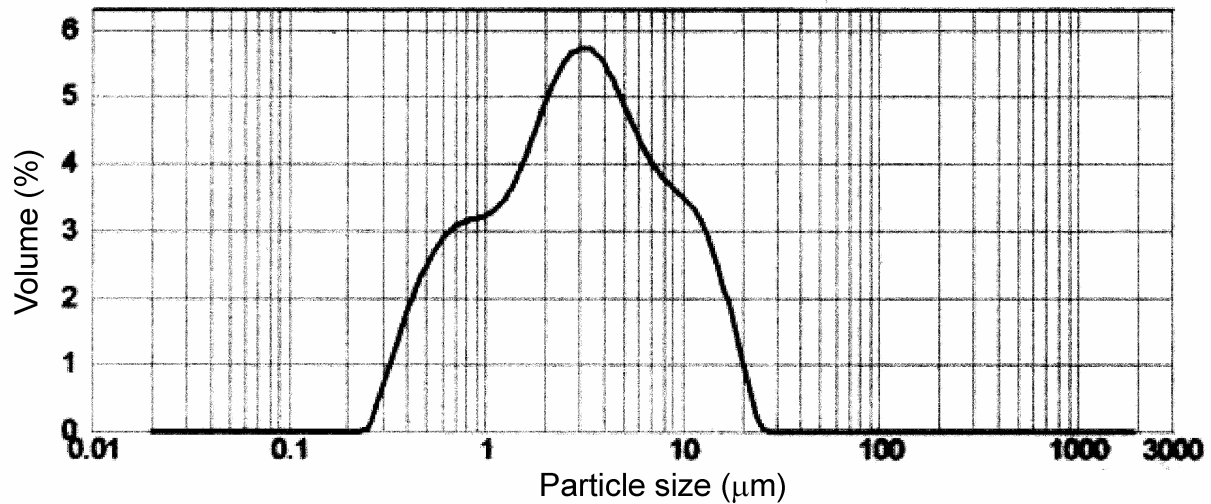


Figure 1. Particle size distribution curve for clay, bentonite.

Table 2. Chemical composition of bentonite clay.

Elements	%(w/w)
SiO ₂	53.99
Al ₂ O ₃	24.08
Fe ₂ O ₃	7.29
TiO ₂	1.07
CaO	0.71
MgO	1.90
Na ₂ O	2.64
K ₂ O	0.06
LOI	8.58

samples for each composite were prepared for each type of mechanical testing to estimate the precision of reported data.

Thermal behaviour was investigated by differential scanning calorimetry (Universal V 4.2E TA Instruments). The samples were cut from each molded sheet of clay composite. About 2.5 mg of the clay composite was placed in an aluminium pan and tested immediately. The amount of clay in the PP clay composite was changed from 0–10 wt%.

The morphology and dispersion in the PP clay composites were studied using scanning electron microscope (LEO 430i) and transmission electron microscope (JEOL JEM 200 CX).

3. Results and discussion

3.1 Characterization of bentonite clay

Chemical analysis of the used clay is shown in table 2. It shows that the bentonite has high iron content (Fe₂O₃ = 7.29) like common Indian bentonites. BET surface area of this clay was low (126 m²/g) compared to standard bentonites (e.g. MMT K10 from Sigma Aldrich), which have higher surface areas (220–270 m²/g).

Figure 1 presents the particle size distribution curve of the bentonite clay. The size distribution appears to be an overlap of three normal distribution curves. The finest fraction is montmorillonite phase since clay fraction usually lies < 1 μ in size. The coarser particles may be composed of quartz and illitic materials with varying degrees of agglomeration. Particle size analysis data shows that volume weighted mean *D*[4,3] of this clay is 4.5 μ. This appears to be higher because montmorillonite particles are usually submicron by nature. As a general rule, as the

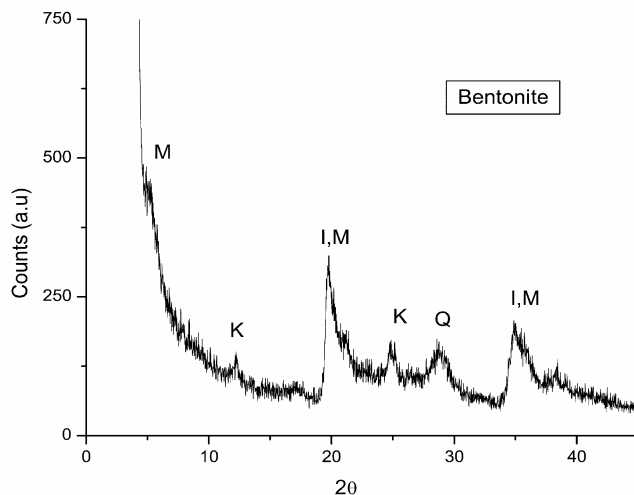


Figure 2. X-ray diffraction pattern of the clay, bentonite.

measured according to ASTM D 256. Hardness properties were investigated by a Shore Durometer in Shore D scale at room temperature according to ASTM D 2240. Three

aspect ratio of the particle increases, sedimentation reports a finer size compared to laser diffraction where size relates to the particle volume. Due to high aspect ratio of the particles, laser diffraction method reports a higher value compared to sedimentation methods.

Figure 2 presents the XRD patterns of the pristine bentonite clay. XRD plots of such clays show the presence of montmorillonite as a major phase. Other minor phases are kaolinite (K), quartz (Q) and illite (I).

Figure 3 presents the DTA–TGA plot of the bentonite clay. The DTA–TGA plots show weight loss due to physically adsorbed moisture around 150°C and weight loss due to lattice water around 550°C. In DTA plot, a characteristic endotherm of montmorillonite that appears around 700°C is also present here. A small endotherm followed by a small exotherm around 900°C are present here, which are characteristic of both montmorillonite and illite (Olphen 1977).

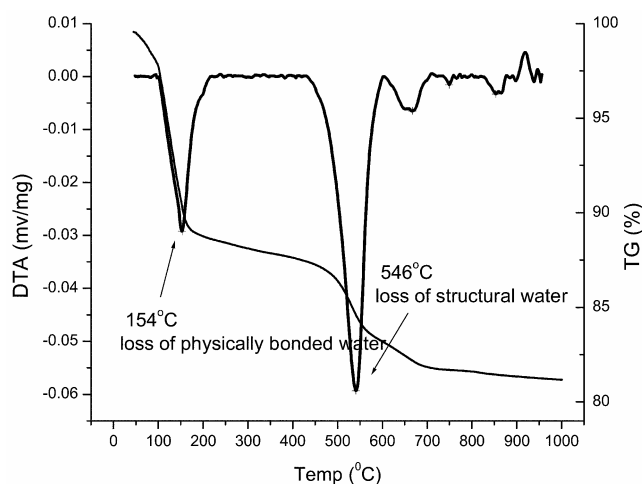


Figure 3. DTA–TGA plot of the clay, bentonite.

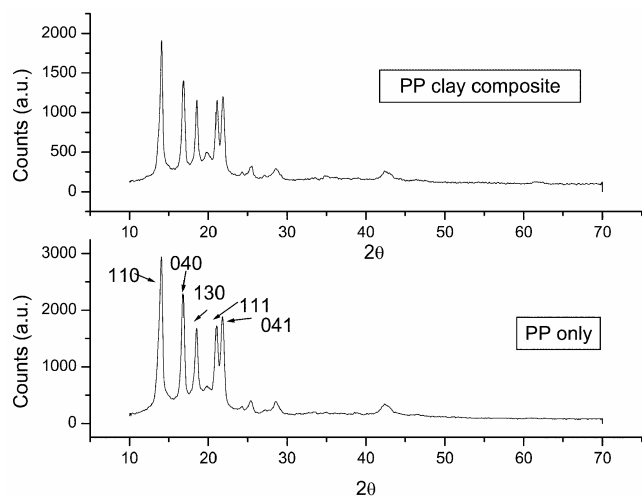


Figure 4. X-ray diffraction pattern of PP only and PP bentonite clay composite.

3.2 Characterization of polypropylene–bentonite clay composite

Figure 4 presents the XRD patterns of one of the 10 mass % bentonite clay composite samples as well as pristine polypropylene. The X-ray diffraction pattern of the PP bentonite clay composite showed that the addition of 10 mass % of bentonite clay did not affect the crystallographic nature of PP, as already observed by others. In both virgin PP and PP with bentonite, the crystal plane of polypropylene is monoclinic, showing reflections assigned to planes (110), (040), (130) and others as indicated in figure 4 (Filho *et al* 2005).

Study of mechanical properties reveals that the change in the respective properties is observed remarkably for 5 mass % of clay loading in the matrix. Figure 5 presents the variation of ultimate tensile strength and modulus with bentonite clay content. For bentonite clay composites,

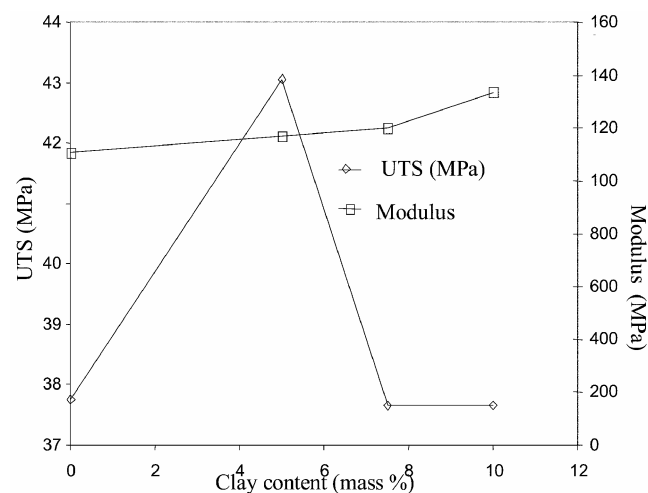


Figure 5. Variation of ultimate tensile strength and modulus with bentonite clay content.

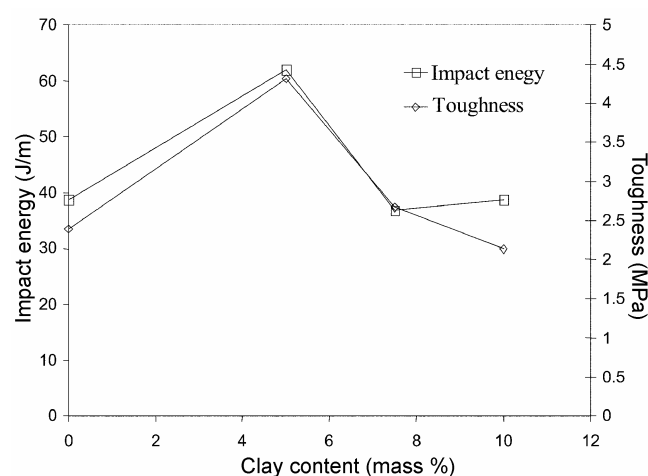


Figure 6. Variation of toughness values and impact energy with bentonite clay content.

tensile strength increased by about 14% for 5 mass % clay composite and after that it remained practically unchanged for higher clay loading. But no significant change in tensile modulus values is observed. Only a slight increase is observed for 10 mass % polymer clay composites. Figure 6 presents variation of toughness values and impact energy with bentonite clay content. Increase in impact strength is observed for 5% clay loading and then the value decreases with clay loading. Similar trend is exhibited in the toughness value plot and the increase in toughness value is about 80% more than that of the neat PP. Improvement in toughness may be due to higher void stresses and improved matrix resistance attributed to finer, more oriented clay particles.

No significant change in hardness properties of the polymer clay composites is observed. Thus the study of mechanical properties reveals that the change in the re-

spective properties is observed remarkably for 5 mass % of clay loading for clay composites. DSC thermograms of all bentonite clay composites (not shown here) exhibited a single melting endotherm and a constant melting temperature ($\approx 164^{\circ}\text{C}$). But there is no significant change in ΔH (J/g) value of PP bentonite clay composites.

The SEM image (figure 7) of the pristine bentonite clay shows an aggregate of montmorillonite platelets, exfoliated during dispersion in water during sample preparation. The fractured surface of a PP bentonite clay composite with 10 mass % of clay (figure 8) shows that clay dispersed in the polymer matrix in aggregates of different sizes, which indicates inhomogeneous distribution of clay in the PP matrix. Unfilled PP (figure 9) has a relatively smooth fracture surface indicating weak resistance to crack propagation. In case of PP composite, fractured surface becomes rougher. Many clay agglomerates are

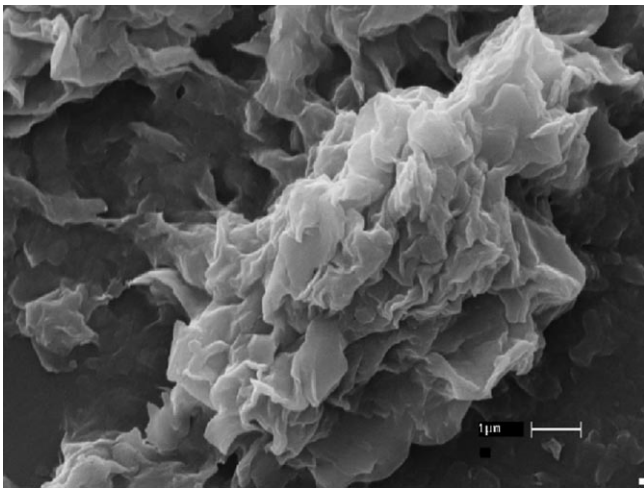


Figure 7. SEM of layered exfoliated structure of bentonite clay.

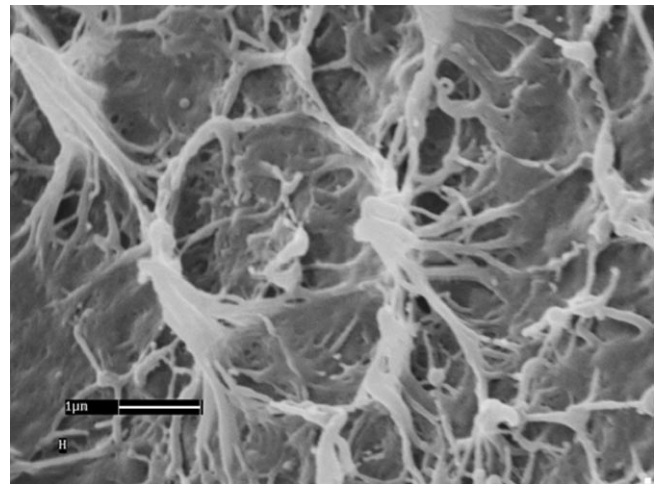


Figure 9. SEM of the fractured surface of only PP matrix.

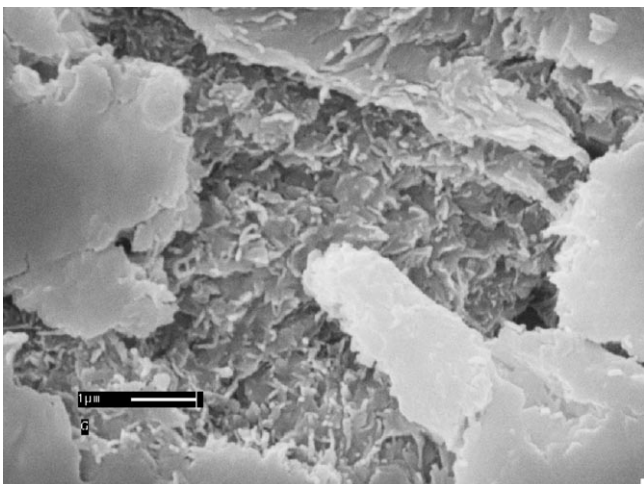


Figure 8. SEM of the fractured surface of PP (10 mass %) bentonites clay composite.

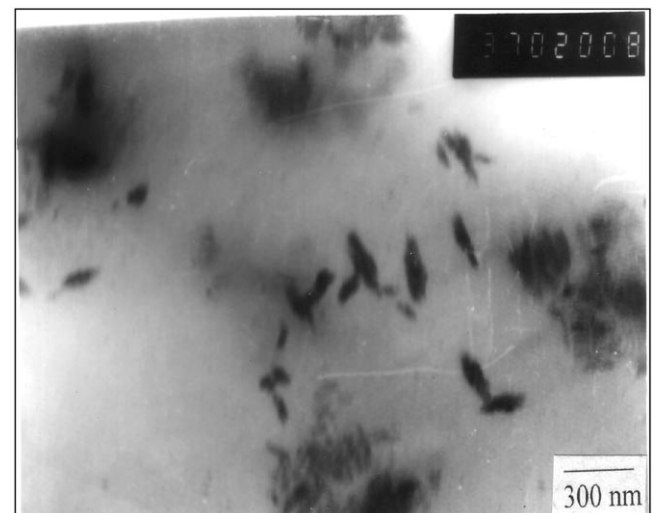


Figure 10. Transmission electron micrograph of PP (5 mass %) bentonite clay composite.

dispersed in the matrix. Thus increased content of clay in the PP composite led to large agglomerates and thus greater probability of debonding due to the poor interfacial adhesion.

Figure 10 presents the transmission electron micrograph of PP bentonite clay composite with 5 mass % of clay. Few clay particles observed are multiple stacks of clay layers although it is observed that intercalation took place in some part of the PP matrix. Such clay dispersion was shown to yield very promising results in terms of mechanical properties (Ton-That *et al* 2004). Thus a mixed morphology with multiple stacks of clay layers and tactoids of different thicknesses are observed in the PP matrix. Thus the TEM image shows that the clay is not evenly dispersed throughout the matrix. In fact, even though some tactoids have been found, most of the clay stacks are confined to clusters.

4. Conclusions

Cheap filler-like bentonite can be effectively used as a good reinforcement for PP matrix even without any modification. Composite was prepared by solution mixing of PP with varying amounts of pristine bentonite clays (5, 7.5, 10 mass %). XRD shows no crystallographic change of the matrix in the composite. SEM study shows a mixed morphology with multiple stacks of clay layers and tactoids of different thicknesses in the PP matrix. TEM study shows that intercalation took place in some parts of the matrix. Significant improvement in tensile strength and toughness value with negligible change for tensile

modulus value was observed. Further it is observed that these improved mechanical properties can be obtained only at low clay loading of 5 mass%. Higher clay loading produced inferior mechanical properties probably due to agglomeration and less interaction between matrix and clay.

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